Morphology, Microstructure, and Mechanical Properties of a Copper Electrodeposit

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Outline

Introduction:

- Electrodeposited copper (you know already)
- The advent of nanoscale materials (you know already)
- Micro- and nanoscale characterization of mechanical behavior is coming along (you know already)
- Atomistic modeling, and molecular dynamics

Characterization of an electrodeposit: "snowball copper"

- SEM
- Diffractometry
- EBSD
- Microtensile

Modeling

Interpretation (including unsolved issues)

Molecular dynamics Introduction, 1/2

Comes in a variety of flavors

Key unifying theme:

Model materials, now necessarily nanoscale materials, by setting up a numerical model with explicit atoms and atomic interactions, and following the behavior

Variations on the theme:

Quantum mechanical or Newtonian*

Has implications on how many atoms can be treated

Bonded or unbonded* atoms

Many of the beautiful and complex images of biological molecules, *e.g.*, proteins, use explicitly bonded models. All bonds are specified. None are created or destroyed. The model just gives the exact position of the interacting atoms.

Etc.

Isotropic* or angle-dependent potentials, and on and on….

Molecular dynamics Introduction, 2/2:

To get elastic constants and vacancy energy of metals correct, *many body interactions* are needed.

Most results presented below: EAM, embedded atom model

(isotropic)

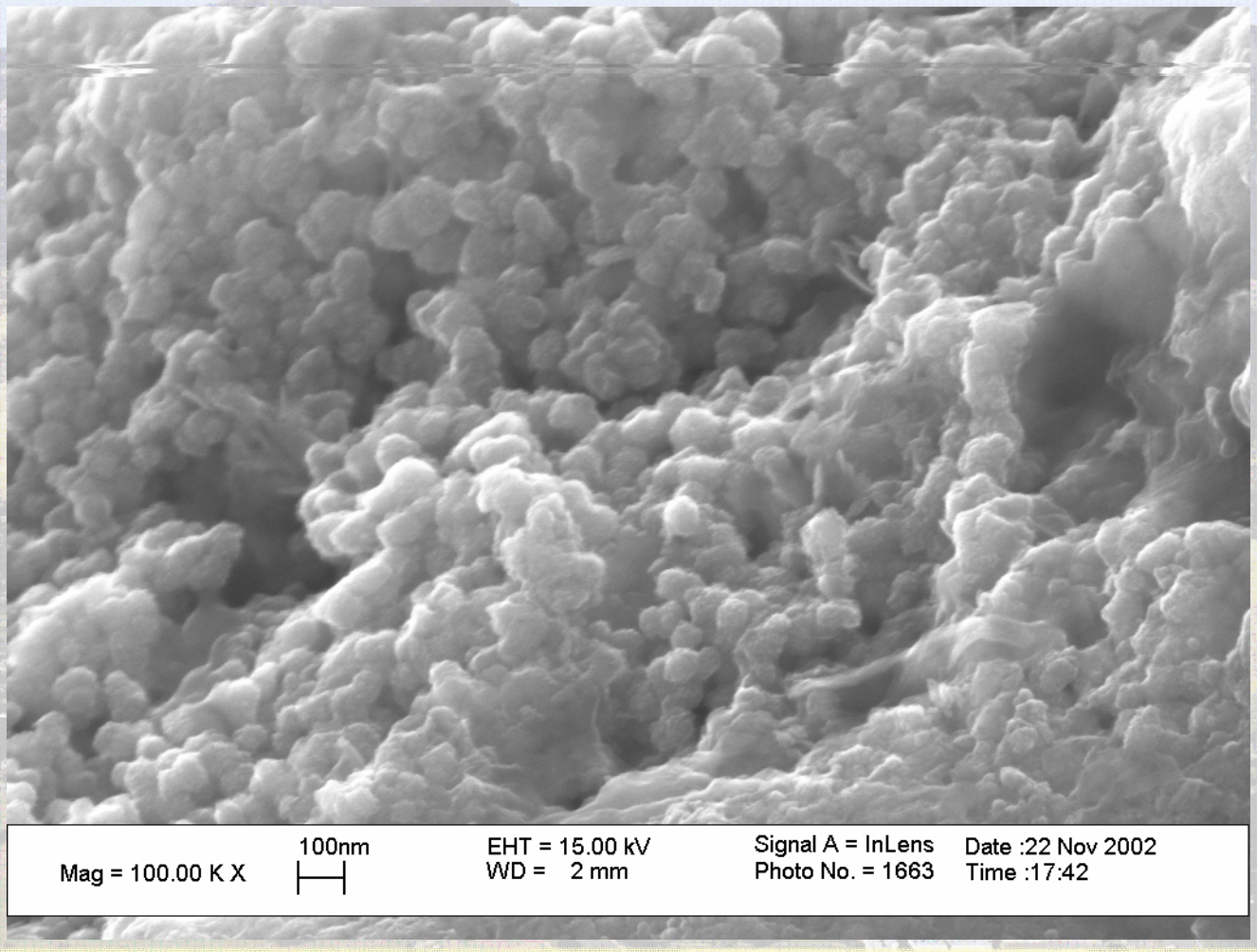
For comparison, also:

Tight binding—second moment model

(isotropic)

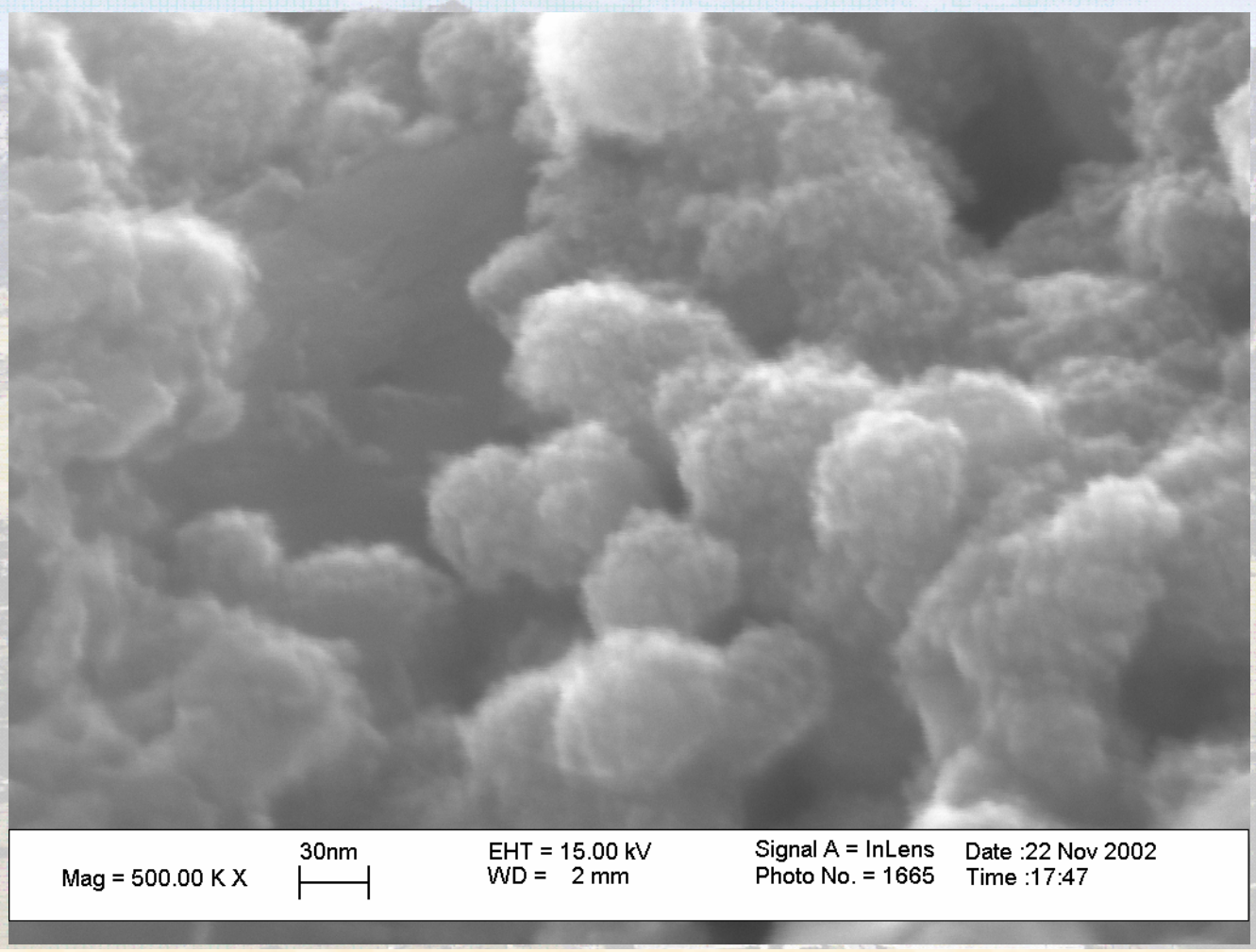
MEAM, modified embedded atom model

(angle-dependent terms)



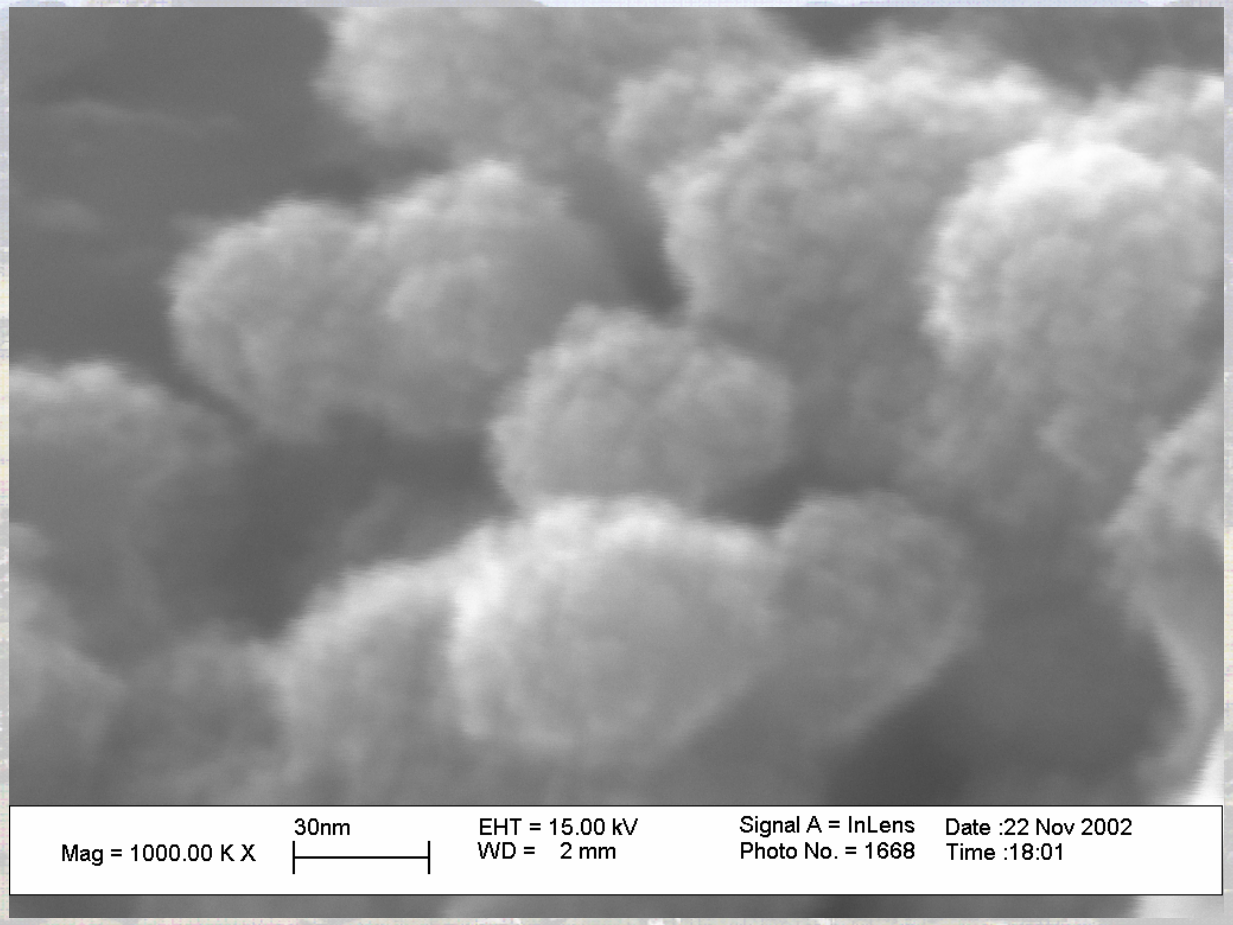
Copper electrodeposited at NIST , 2.5 µm thick

Note appearance: an agglomeration of spheroids

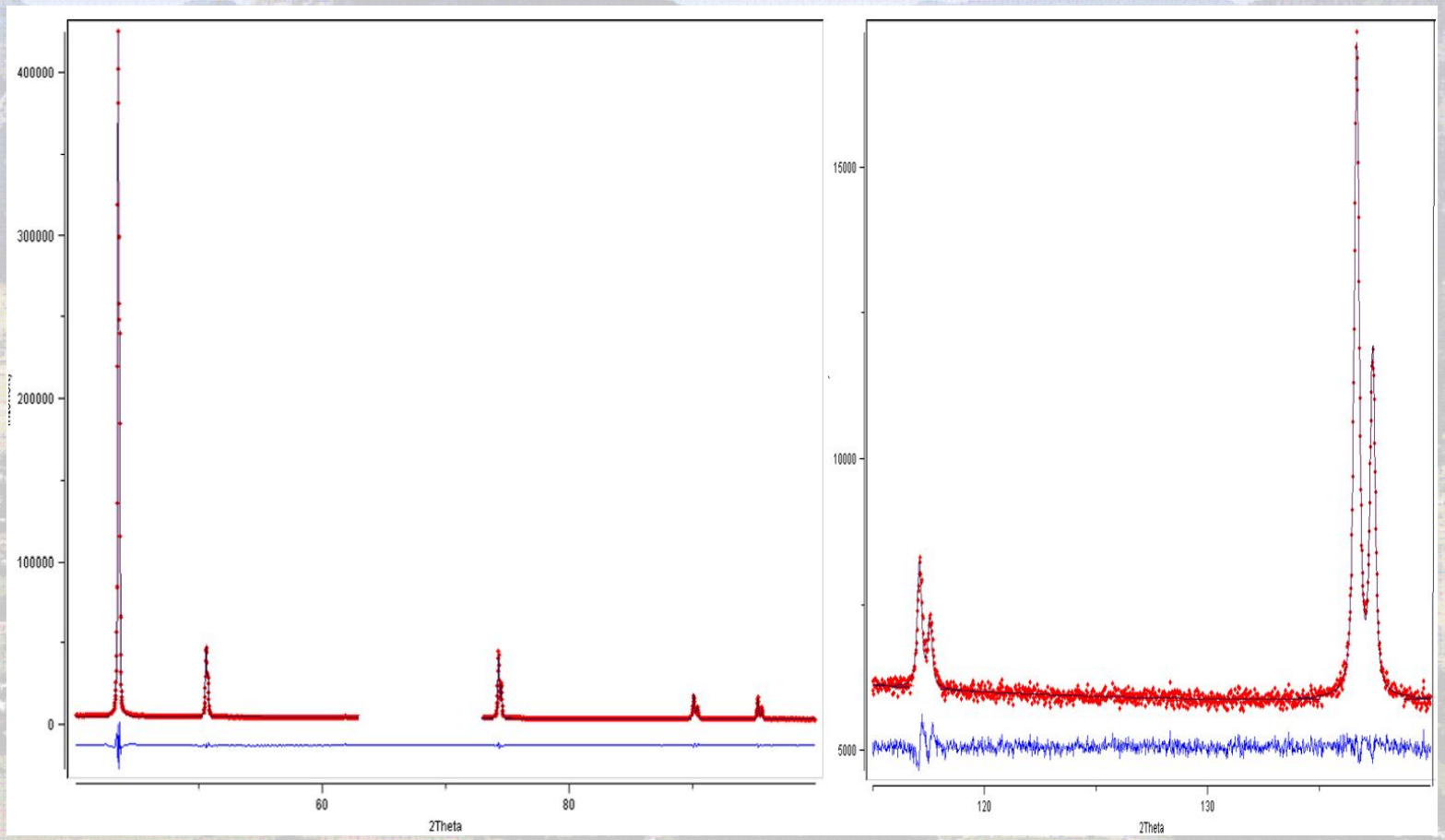


Micrograph at 500 kX clearly shows spheroids

Diameter approximately 60 nm



Micrograph at **1 million X** hints at substructure of the spheroids



Diffractometer data (sharp lines!)

Diffractometry results

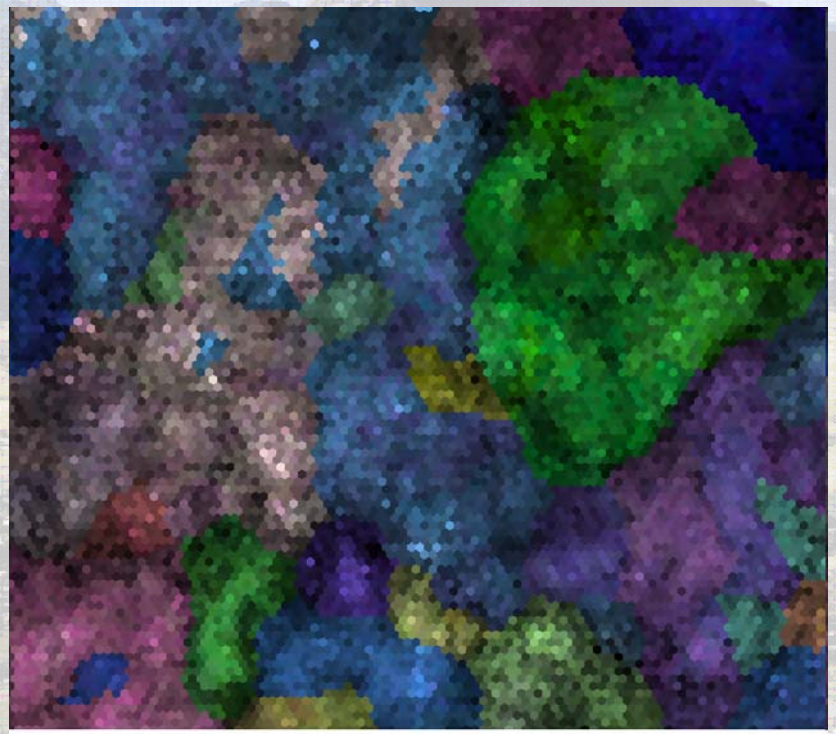
Lattice parameter: nominal

Texture: strong (111)

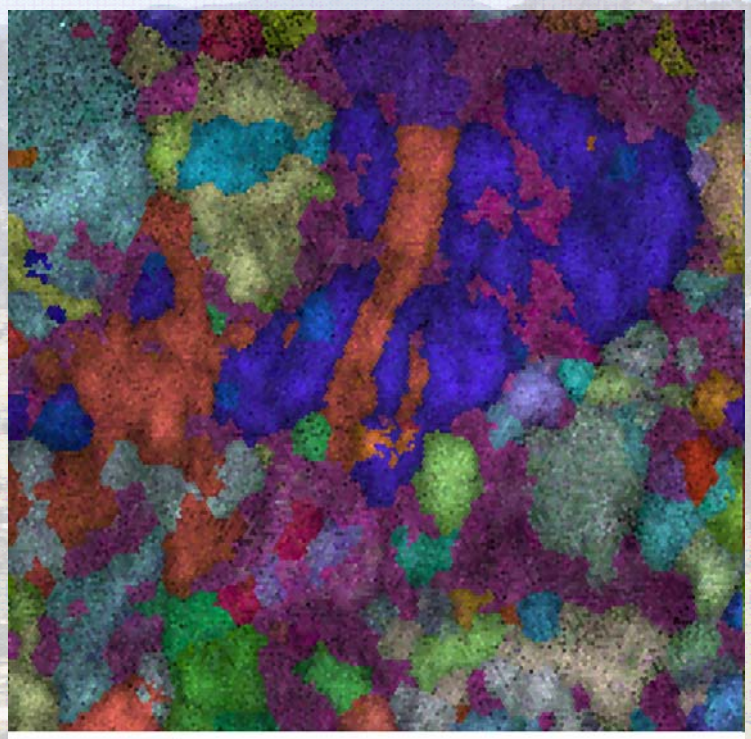
Residual strain: Small in plane, none out of plane

Domain size: 280 ±110 nm (surprisingly large!!!, based on fine lines)

Acknowledgement: Goran Stefanic



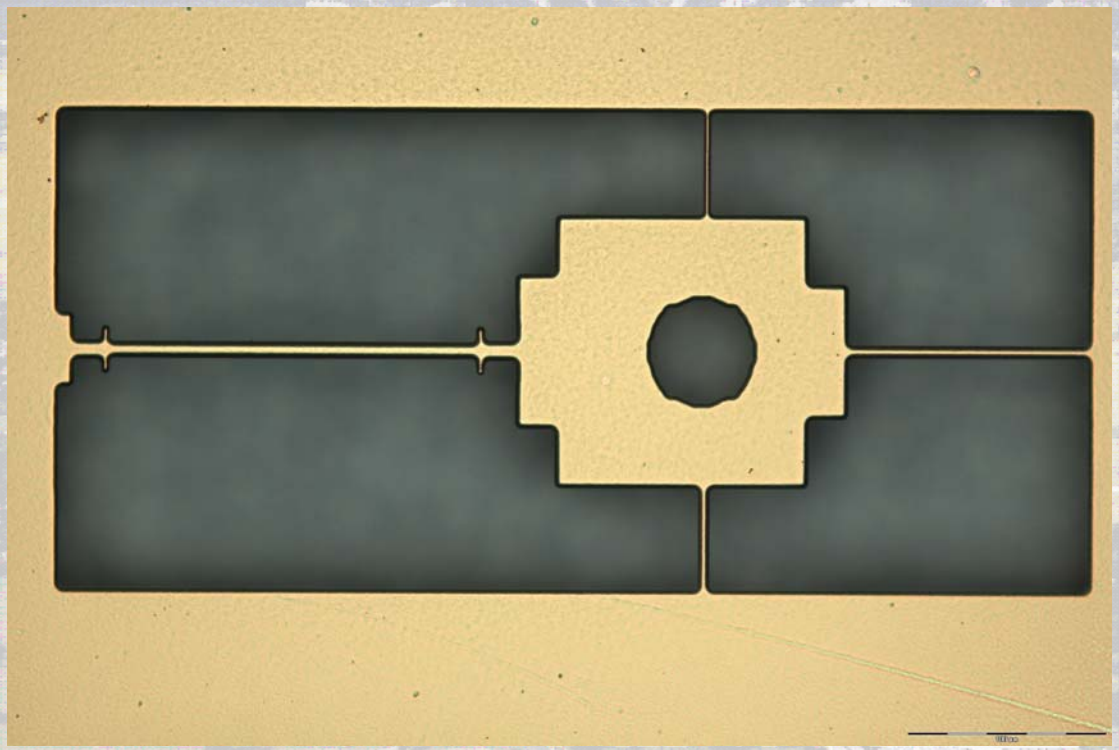
2.00 µm = 20 steps IQ 26.152...76.427, IPF [001]

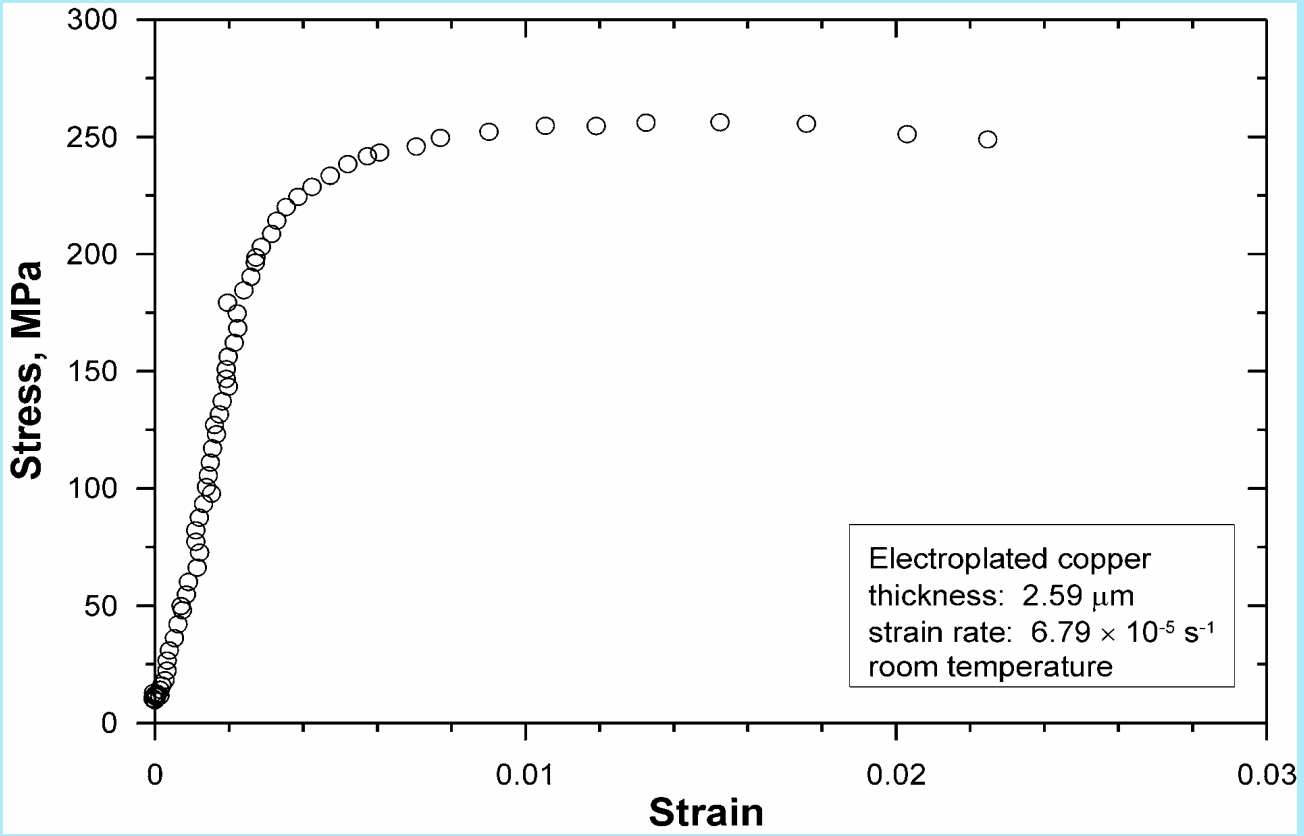


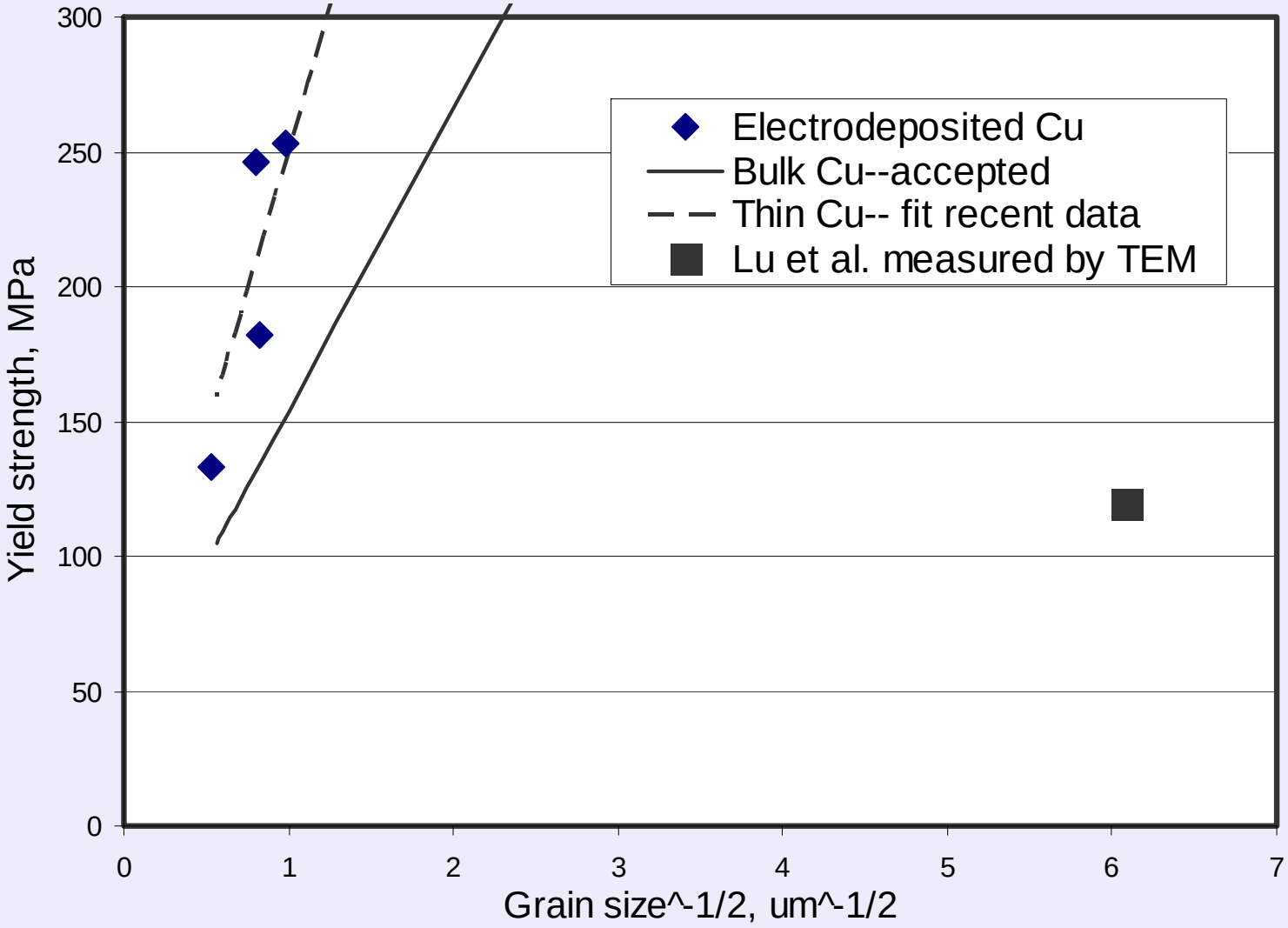
2.00 µm = 40 steps IQ 18.885...45.05, IPF [001]

EBSD scans show grain size of the order of 1.5 µm (intercept)

Microtensile results




300
250
200
150
100
50
0
Stress, MPa
0
0.01
0.02
0.03
Strain
Electroplated copper
thickness: 2.59 μm
strain rate: 6.79 × 10-5 s-1
room temperature


Yield strength, MPa
300
250
200
150
100
50
0
0
1
2
3
4
5
6
7
Grain size^-1/2, um^-1/2
Electrodeposited Cu
Bulk Cu--accepted
Thin Cu-- fit recent data
Lu et al. measured by TEM

Interpretation

Hypothesis:

Spheroids formed in the electroplating solution, somewhere between the anode and the cathode (the growing electrodeposit)

Then the spheroids agglomerated

* * *

So far no contradiction with atomistics: atoms always want to stick together

One expects the spheroid size to be controlled by the details: current density, distance to cathode, solution concentration, etc.

Issues:

Details of the agglomeration mechanism.

Is some force needed to drive the spheres together, for example, a force from the electrical potential?

Does the solution play a big role in the agglomeration?

Why are the mechanical properties so normal, except:

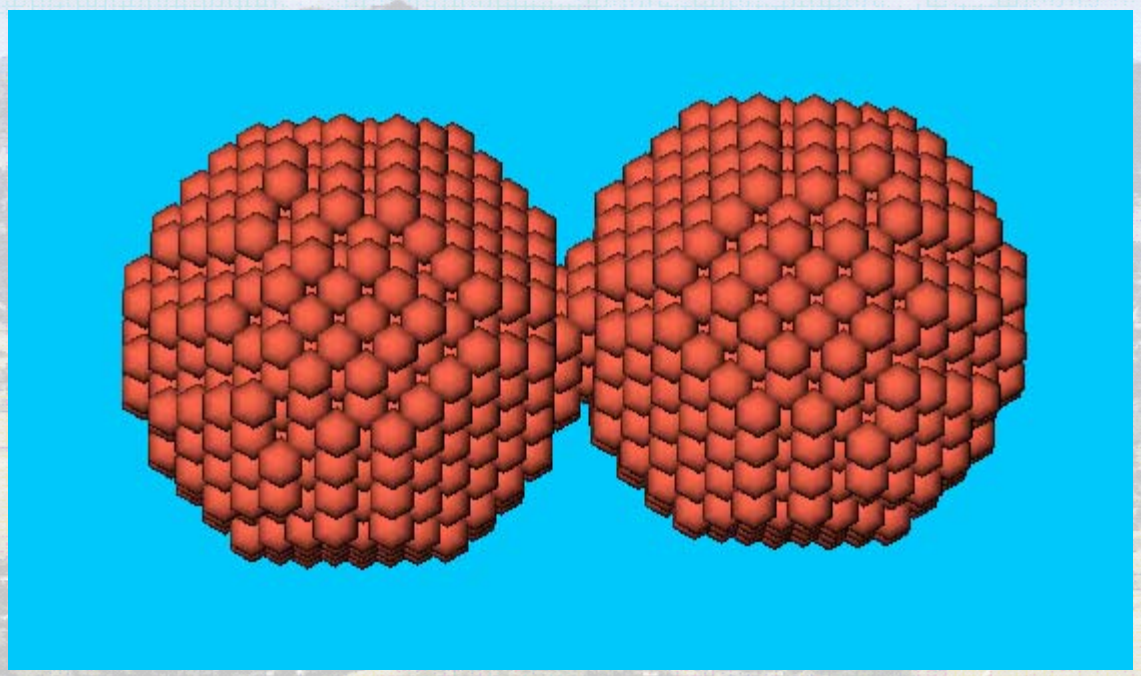
The modulus is low;

Lu et al. material (2 mm thick) said to be superplastic.

Agglomeration of spheres is a favorite topic in MD – I personally find it practically irresistible

Earliest reference I have found:

"Sintering processes of two nanoparticles: a study by molecular dynamics simulations," H. Zhu and R. Averback, *Philosophical Magazine Letters*, 1996

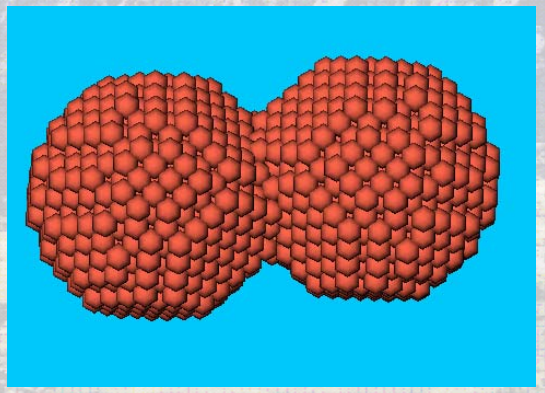


Assume that perfect face-centered-cubic (fcc) spheres form in the electroplating solution.

Assume two such spheres approach each other

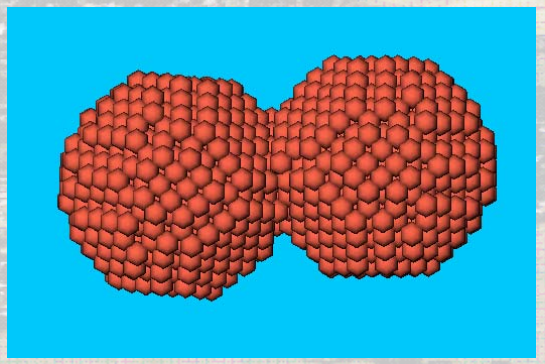
Model: ~1000 atoms per sphere, realistic (EAM, embedded atom model) potential, cutoff after 3rd neighbors.

Results after 9×10^{-12} s (9 picoseconds):

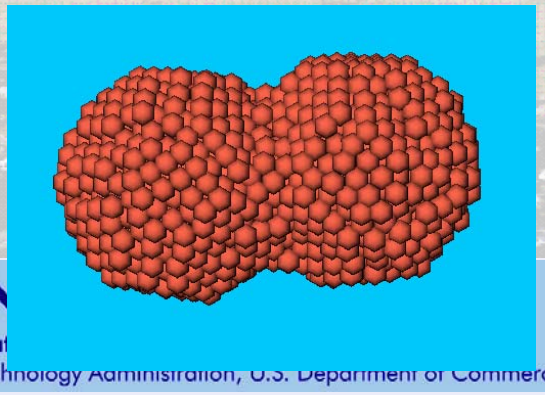


Temp., K:

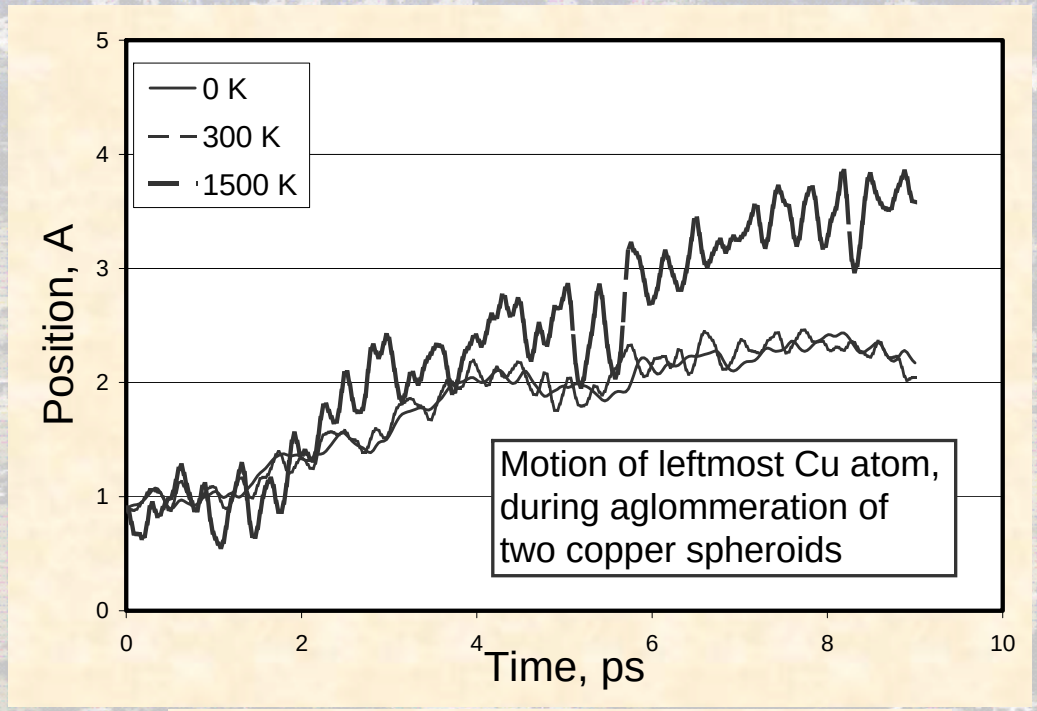
0



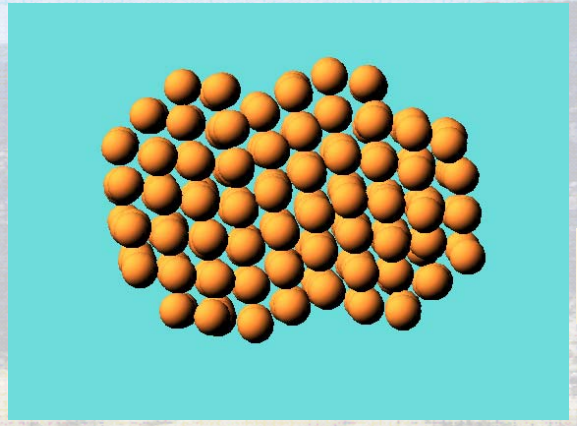
300



1500



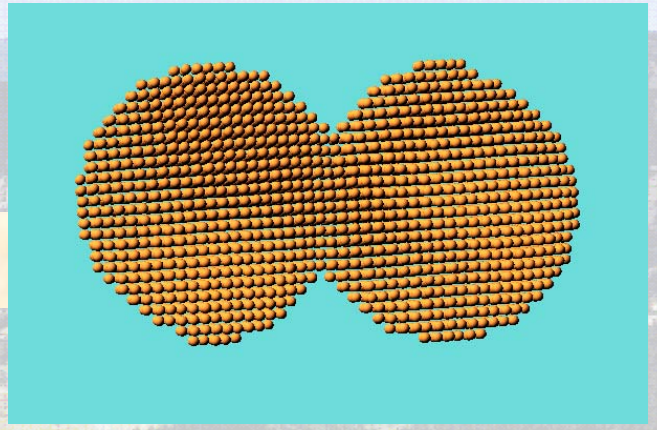
Result: Spheroids can agglomerate at room temperature without electrical forces or solvent effects

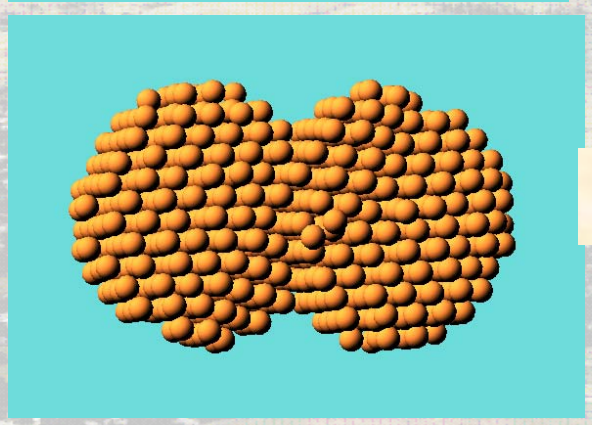


Atoms per initial sphere

140

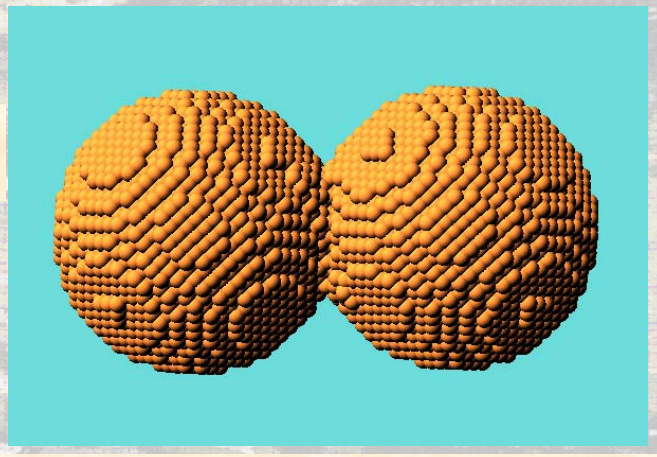
3604

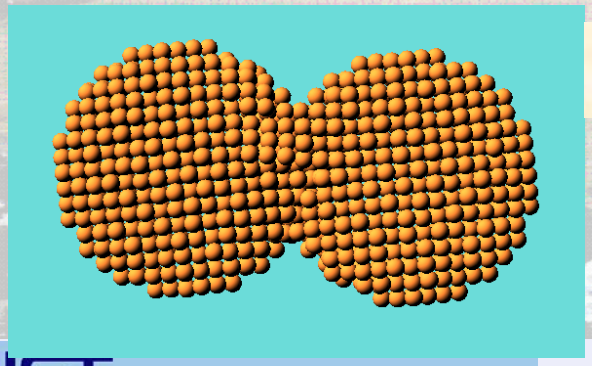




456

8628

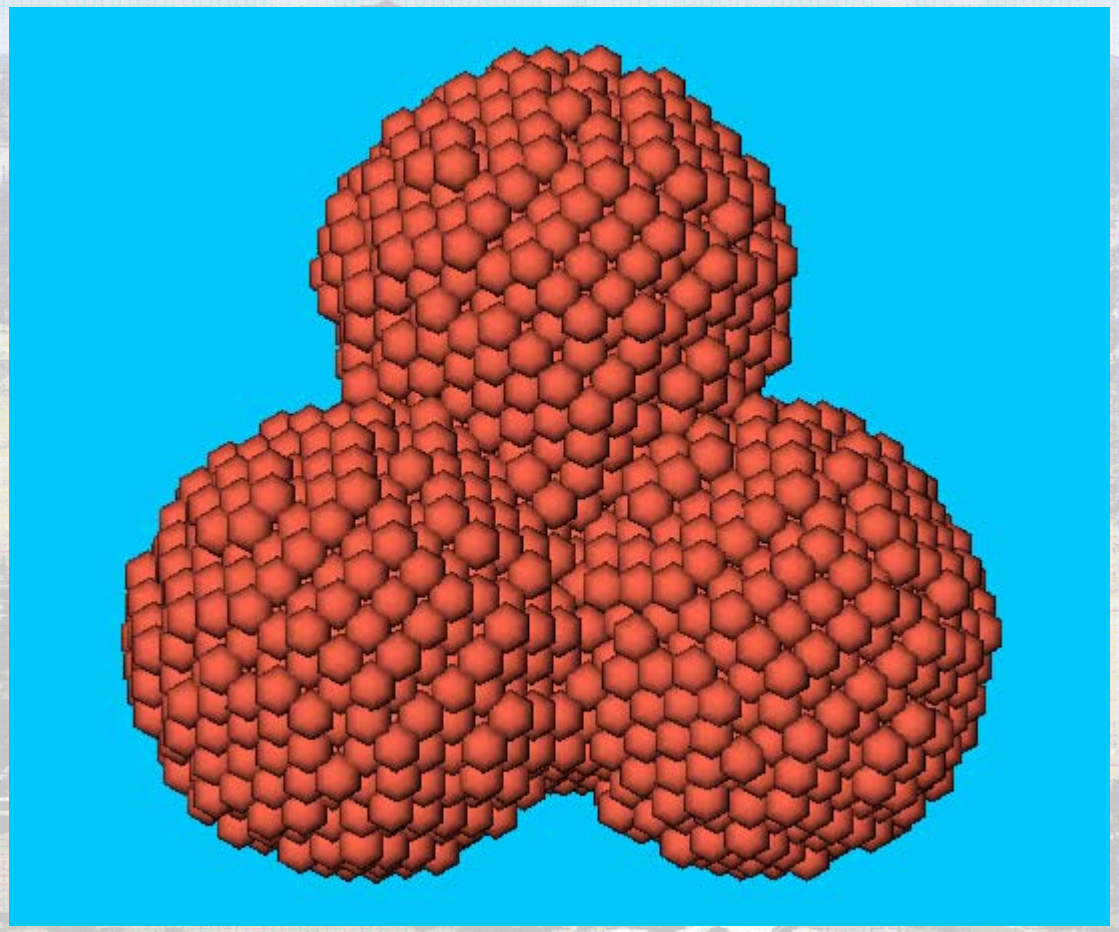




1088

EAM modeling:

Size effect in metal sphere agglomeration, 0 K



Model is extensible to 4 ~1000 atom spheres at 300 K

This simulation required 7 m 23 s on a desktop PC

Zhu and Averback and other references, and my modeling, find:

Persistent low energy grain boundaries between spheroids.

This contradicts the experimental results--relatively large grains.

To date, MEAM and TB—SM models appear to behave the same way.

This suggests some care will be required in direct application of MD to nanoscale structures.

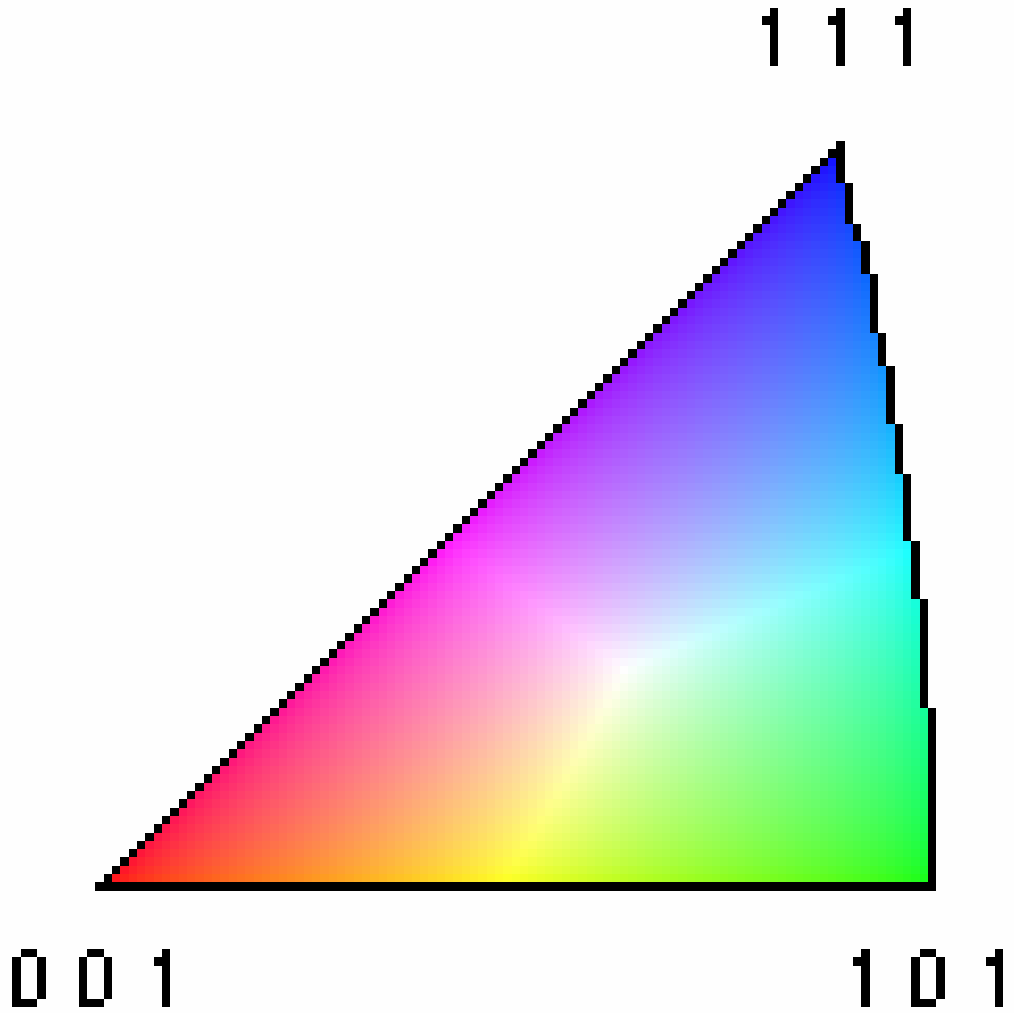
Conclusion:

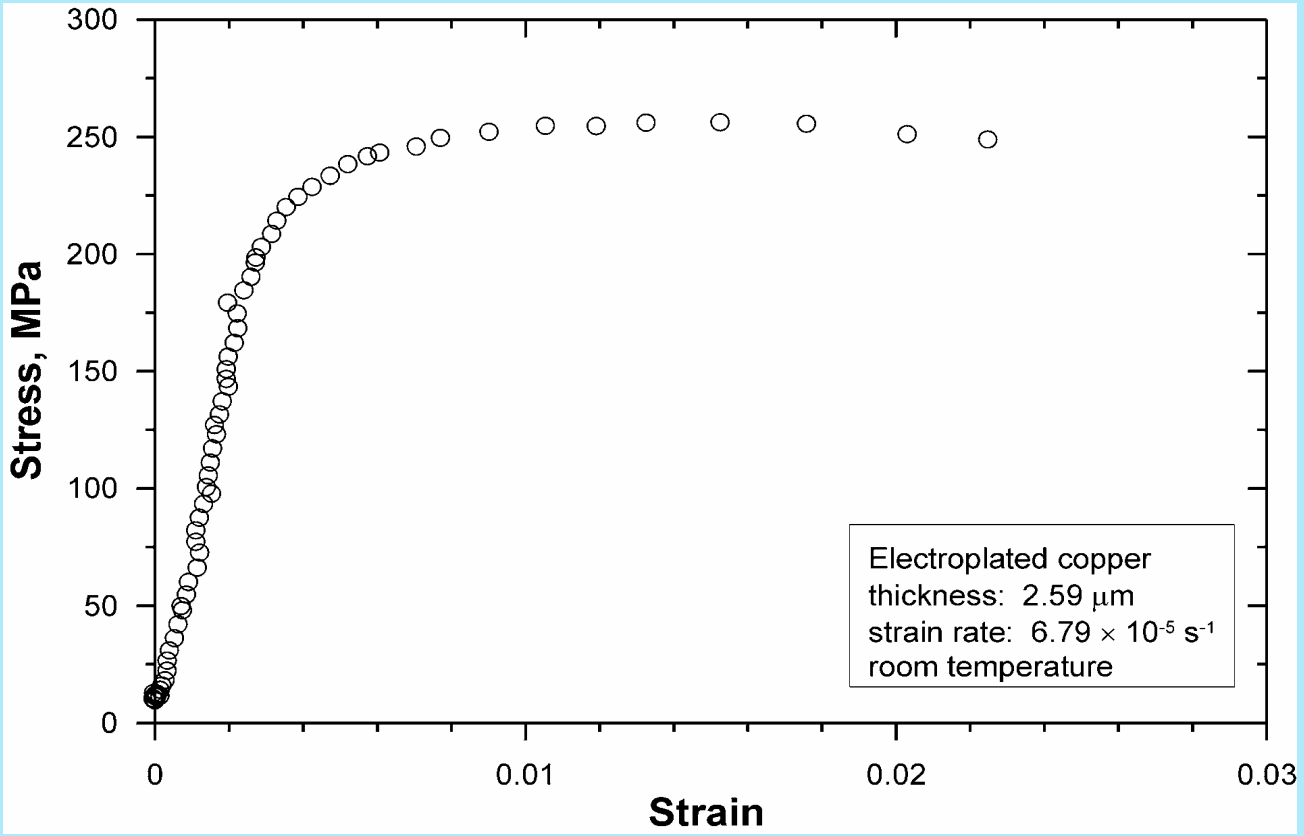
Copper electrodeposits have interesting and complex small-scale morphology;

Mechanical properties surprisingly consistent among different electrodeposited films, and not markedly different from bulk scaled with Hall-Petch;

Atomistic modeling rationalizes spheroid agglomeration, but so far grain growth not handled, possibly because of:

- Time scale
- Interatomic potential




300
250
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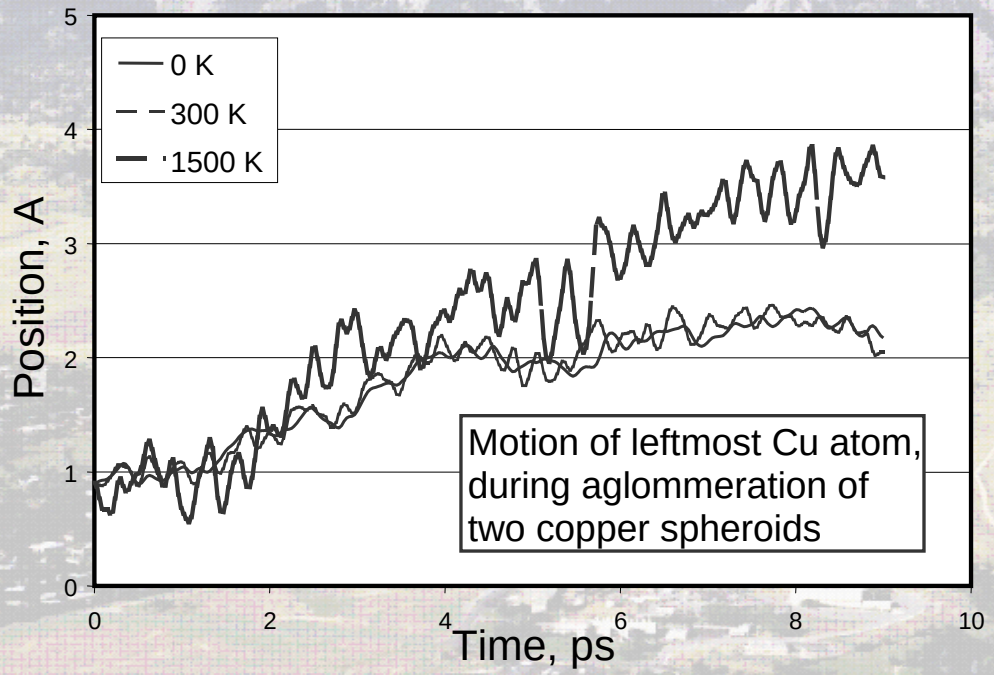
0 K
300 K
1500 K
Position, A
Time, ps
0
1
2
3
4
5
0
2
4
6
8
10
Motion of leftmost Cu atom, during aglommeration of two copper spheroids